Ni impurity induced enhancement of the pseudogap in cuprate high T_c superconductors

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Abstract

The influence of magnetic Ni and non-magnetic Zn impurities on the normal state pseudogap (PG) in the c-axis optical conductivity of $NdBa_2\{Cu_{1-y}(Ni,Zn)_y\}_3O_{7-\delta}$ crystals was studied by spectral ellipsometry. We find that these impurities which strongly suppress superconductivity have a profoundly different impact on the PG. Zn gives rise to a gradual and inhomogeneous PG suppression while Ni strongly enhances the PG. Our results challenge theories that relate the PG either to precursor superconductivity or to other phases with exotic order parameters, such as flux phase or d-density wave states, that should be suppressed by potential scattering. The apparent difference between magnetic and non-magnetic impurities instead points towards an important role of magnetic correlations in the PG state.

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The unconventional normal-state (NS) properties of the cuprate high T_c superconductors (HTSC) are a key issue in the search for the superconducting (SC) pairing mechanism. A prominent feature is the so-called pseudogap (PG) phenomenon which prevails in under-doped samples where it gives rise to a gradual and incomplete suppression of the low-energy spin and charge excitations well above the SC transition temperature, T_c. It was first discovered by nuclear magnetic resonance (NMR) [1] and subsequently identified in specific heat [2], angle-resolved photo-emission (ARPES) [3], and also in optical measurements [4]. In the latter it appears as a gap-like suppression of the far-infrared (FIR) c-axis conductivity perpendicular to the CuO_2 planes. The characteristic energy- and temperature (T) scales of the PG increase with underdoping whereas on the overdoped side they merge with or fall below the ones of the SC energy gap [3,5]. Numerous models have been proposed to account for the PG phenomenon. The most influential ones can be divided into two categories. In the first one, the PG is related to a precursor SC state where macroscopic phase coherence is inhibited by thermal phase fluctuations [6] or pair condensation is delayed to much lower T than pair formation (Bose-Einstein-condensation scenario) [7]. The second class assumes a distinct kind of order that may even compete with SC [8]. Proposals include conventional and exotic spin- or charge density wave states [9–12], the stripe scenario [13], spin singlets in the spin-charge separation scenario [14] or lattice driven instabilities [15].

A major obstacle for the identification of the PG state is that its low T properties are obscured by the response of the SC condensate. This problem can be overcome if SC order is suppressed either with a large magnetic field or by means of impurities within the CuO_2 planes (Zn or Ni for Cu) that cause strong pair-breaking. The former approach requires extremely large fields and is thus not viable in combination with spectroscopic techniques that access the relevant electronic energy scales. The latter approach has been limited to samples with rather low impurity content and thus minor T_c suppression [16].

Here we report on the evolution of the PG in the optical c-axis conductivity of $(Sm,Nd)Ba_2\{Cu_{1-y}(Ni,Zn)_y\}_3O_{7-\delta}$ single crystals. Up to 9 % Zn and 17 % Ni per Cu atom have been incorporated allowing for a full suppression of SC even at optimum doping.

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We find that non-magnetic Zn impurities and magnetic Ni impurities, both of which strongly suppress SC, have a profoundly different impact on the PG. The non-magnetic Zn impurities lead to a slow and inhomogeneous PG suppression, whereas the magnetic Ni impurities are beneficial and strongly enhance the PG phenomenon. Ni substitution restores a normal state PG even in optimally doped and slightly overdoped samples where the PG is otherwise absent. Our observations are at variance with theories that relate the PG to a precursor SC state. Similar arguments apply for the exotic order parameters of the flux-phase or d-density wave states where potential scattering from impurities also gives rise to destructive interference effects. Our data support the point of view that magnetic correlations play a prominent role in the PG formation.

High quality $(Sm,Nd)Ba_2\{Cu_{1-y}(Ni,Zn)_y\}_3O_{7-d}$ single crystals were grown with a flux method under reduced oxygen atmosphere to avoid the substitution of RE ions on the Ba site [17]. Zn and Ni contents were determined by energy dispersive x-ray (EDX) analysis. The use of rare earth ions with a large ionic radius (Nd or Sm) was found to assist the incorporation of higher amounts of Zn and Ni impurities. The SC transitions were determined by SQUID magnetometry. The quoted values of T_c and ΔT_c correspond to the midpoint and 10 to 90 % width of the diamagnetic transition. The T_c suppression closely follows the reported trend for Zn impurities [18] while for the Ni-impurities it is significantly faster than in Y123 [19,20]. Assuming a similar T_c suppression rate for Zn and Ni impurities in the CuO_2 planes, we deduce that about half the Ni impurities reside in the planar Cu sites as opposed to the chain site which is favored in Y123 [19,20]. Zn is known to enter exclusively the planar site even in Y123. By annealing in flowing O_2 gas and subsequent rapid quenching into liquid nitrogen we prepared a series of crystals with different Zn and Ni concentrations but identical oxygen content. It was shown by thermo-electric power (TEP) [21] and NMR [19,20] that Zn substitution leaves the hole doping state, p, of the CuO_2 planes unaffected. We performed TEP measurements on our crystals which establish that the Ni impurities also do not significantly alter the hole doping state, p.

The ellipsometry experiments were performed at the infrared (IR) beamline at the ANKA

synchrotron at Forschungszentrum Karlrsuhe, Germany and with a laboratory-based setup [22]. Ellipsometry measures directly the complex dielectric function without a need for Kramers-Kronig analysis. It is a self-normalizing technique that allows one to determine very accurately and reproducibly the dielectric function and, in particular, its T-dependent changes.

In Figs. 1a to 1c we present spectra of the real part of the c-axis conductivity, σ_{1c}, below 2500 cm^{-1} (806 cm^{-1} ≜ 100 meV) for Ni substituted NdBa$_2$Cu$_{3-y}$Ni$_y$O$_{6.8}$ single crystals with y=0, 0.03, 0.06 and 0.12. The crystals were annealed at 520 °C in flowing O$_2$ and were underdoped with T$_c$=65(4) K for y=0, T$_c$=20(5) K for y=0.03, and T$_c$<2 K for y=0.06 and 0.12. It is well established that a slightly higher oxygen content is required for Nd123 as compared with Y123 in order to obtain the same doping state in the CuO$_2$ planes [23]. The TEP data indicate an almost constant hole doping state ranging from p≈0.1 at y=0 to p≈0.11 at y=0.17. Figure 1a shows that the characteristic spectral features of the Ni-free crystal closely resemble those of similarly underdoped Y123 [4,5]. The narrow peaks correspond to the well known IR-active phonon modes of the 123 structure. A broader mode near 420 cm^{-1} that develops in the SC state can be attributed to a transverse Josephson resonance mode [24]. Only the so-called rare-earth mode exhibits a significant red shift from 190 to at 175 cm^{-1} that is consistent with the mass ratio of Nd and Y. In the following we are mostly concerned with the underlying broad electronic response. In particular, we focus on the suppression of the electronic conductivity below ∼1100 cm^{-1} which develops already in the NS. A corresponding gap feature was previously observed in underdoped Y123 and has been associated with the PG [4]. It was shown to exhibit a similar magnitude, spectral shape and doping dependence as the PG that emerges from other spectroscopic experiments like ARPES or tunneling spectroscopy [5]. It has a gradual onset at $\omega^{PG} \approx 2\Delta^{PG}$ (marked by arrows) that is characteristic of a k-space anisotropy of the underlying order parameter. Our most important result is that the energy scale of the PG in the c-axis conductivity becomes strongly enhanced upon Ni substitution, contrary to the naive expectation that impurities like Ni should reduce or at least wash out the corresponding gap features. This

is apparent in Figs. 1a to 1c where ω^{PG} increases continuously from 1150 cm^{-1} at y=0.0 to about 2050 cm^{-1} at y=0.12. The evolution of ω_c^{PG} as a function of Ni content for the entire series is displayed in Fig. 1d. We emphasize that the TEP data establish a nearly constant hole doping upon Ni substitution, if at all p exhibits a slight increase. The dramatic Ni induced increase in ω^{PG} thus cannot be explained in terms of a very large Ni-induced hole depletion. We also note that the corresponding in-plane response remains metallic even at y=0.17, albeit with a largely enhanced scattering rate (not shown here).

The spectra for a series of correspondingly underdoped NdBa$_2$Cu$_{3-y}$Zn$_y$O$_{6.8}$ crystals with y=0.0 (T$_c$=65(5) K), 0.06 and 0.09 (T$_c$<2 K) are displayed in Figs. 1e and 1f. The non-magnetic Zn impurities have a profoundly different impact on the PG phenomenon. The PG onset frequency ω^{PG} exhibits a slight decrease from 1150 cm^{-1} at y=0 to 890 cm^{-1} at y=0.09 (solid squares in Fig. 1d) consistent with previous reports on moderately Zn-substituted Y123 [16]. In addition, the PG apparently fills in and becomes less pronounced upon Zn substitution. This behavior is suggestive of an inhomogeneous scenario where the PG is locally suppressed around Zn-impurities while it remains virtually unaffected in remote regions. It agrees with scanning tunneling microscopy (STM) data on lightly Zn substituted Bi2212 where the spectral gap was locally suppressed in the vicinity of the Zn impurities [25]. In contrast, for the Ni impurities there is no indication for such a spatially inhomogeniety. Especially at high Ni content our spectra even suggest that the PG develops towards a real gap since σ_{1c}^{el} becomes almost fully suppressed at nonzero frequency. The continuous increase of ω^{PG} indeed suggests that the Ni impurities interact with the PG correlations over a sizeable length scale well beyond the nearest neighbor distance. A corresponding increase of the energy gap was not observed in previous STM experiments on very lightly Ni substituted samples [26]. We hope that our data will stimulate STM or ARPES experiments on heavily Ni-substituted crystals.

Our observations provide important information regarding the relevance of several PG models. Firstly, the apparent Ni impurity-induced enhancement of the PG energy scale is at variance with proposals that a precursor SC state lacking macroscopic phase coherence is at

the heart of the PG phenomenon [6]. The Ni impurities (similar to Zn) give rise to sizeable potential scattering; the magnetic scattering is considerably weaker and plays only a minor role in the T_c suppression [19,20,26,27]. The potential scattering mixes states with opposite sign of the d-wave SC order parameter and thus gives rise to destructive interference resulting in a strong T_c suppression and also in a reduction of the magnitude of the energy gap. While a strong-coupling scenario may explain a fairly weak impurity-induced PG suppression as observed for the Zn impurities [28], it does not account for the observed drastic increase of the PG energy scale upon Ni substitution. Similar arguments apply for models that account for the PG in terms of competing order parameters with exotic symmetry like the flux phase or d-density wave states, which also exhibit a sign change in k-space or real-space [11,12]. Potential scattering from the Ni impurities should be deleterious for these order parameters. It is furthermore difficult to explain how the energy scale of conventional charge or spin density waves states [9,10], which rely on the nesting condition at the Fermi-surface, can be so strongly enhanced by Ni impurities which broaden the electronic states and thus tend to weaken the nesting.

While our surprising results allow us to rule out several influential PG models, it remains an open question how the magnetic Ni impurities give rise to such a dramatic increase of the PG energy scale. The stunning difference between magnetic Ni impurities and non-magnetic Zn-impurities points towards an important role of magnetic correlations. Non-magnetic Zn^{2+} (S=0) impurities are known to disrupt the network of AF exchange bonds. While low Zn concentrations (< 2 %) may induce magnetic correlations on nearest or next nearest neighbor Cu sites, these vanish rather rapidly at higher Zn content [29]. Our unpublished μSR experiment establish that the magnetic Ni^{2+} impurities (S=1) progressively strengthen the Cu spin correlations giving rise to a spin-freezing transition even in optimally and slightly overdoped samples. This hints at a prominent role of short-range AF spin correlations in the pseudogap formation. Further neutron scattering studies of the magnetic excitations in highly Ni-substituted samples [30], in particular, in the relevant energy range of 50-100 meV might allow one to further clarify the relationship with the PG phenomenon.

A related question is whether the Ni-impurities on the Cu(2) planar or Cu(1) chains sites are responsible for the PG enhancement. We tried to resolve this issue by investigating a pair of crystals with y=0.06 where the relative Ni occupation was modified by a high temperature annealing treatment (940° C in O_2 as compared to 920° C in 0.2 % O_2) prior to annealing at 520° C. The former sample should contain an appreciably higher Ni-content on the chains. However, we could not observe any significant shift in ω^{PG} which indicates either that we did not manage to induce a sizeable redistribution of Ni between plane and chain sites, or else that magnetic impurities on plane and chain sites tend to enhance the PG correlations. Note that the final answer to this question will not affect our main conclusions concerning the validity of the various PG models, which rely solely on the well established fact that Ni impurities on Cu(2) sites give rise to considerable potential scattering and thus should suppress rather than enhance a PG order parameter with an exotic symmetry.

Another interesting issue concerns the doping dependence of the PG phenomenon in the Ni substituted samples. In the pure samples the normal state PG vanishes at optimum doping, while for overdoped samples the energy gap formation coincides with T_c [4,5]. The SC energy gap thus obscures the evolution of the PG. In particular, it does not allow one to explore whether the PG merges with the SC one extending well into the overdoped regime, or whether it vanishes shortly above optimum doping as was suggested based on specific heat and NMR data [8]. In the following we show that our optical data support the latter scenario. Displayed in Fig. 2 are the c-axis optical spectra for optimally doped but non-superconducting $SmBa_2Cu_{2.86}Ni_{0.14}O_7$ (p$\approx$ 0.16) and overdoped $Sm_{0.86}Ca_{0.14}Ba_2Cu_{2.88}Ni_{0.12}O_7$ with p$\approx$ 0.2 (from TEP). Figure 2a shows that Ni substitution restores a pronounced PG with $\omega^{PG} \approx$2200 cm^{-1} in the optimally doped crystal. For the overdoped crystal, as shown in Fig. 2b, there remains only a trace of a PG whose energy scale furthermore is strongly reduced to $\omega^{PG} \approx$700 cm^{-1}. The rapid decline of the PG energy scale on the overdoped side lends support to models which relate the onset of the PG correlations to a critical point that is located well within the SC dome [8] (and thus hidden in pure samples).

In summary, we have investigated how the normal-state pseudogap (PG) in the c-axis optical conductivity is affected by magnetic Ni and non-magnetic Zn impurities. Most surprisingly, we find that the Ni impurities strongly increase the energy scale of the PG and restore a PG even in optimally and slightly overdoped samples. Our observations are at variance with theories that relate the PG to precursor superconductivity where the PG should not be enhanced by impurities that lead to potential scattering. They also conflict with models of competing phases with exotic order parameters that are susceptible to destructive interference effects from potential scattering, such as flux phase or d-density wave states. Our results indicate that magnetic correlations play an important role in the PG phenomenon. In particular, our data highlight that substitution of magnetic Ni impurities provides a unique opportunity to investigate the ground state properties of the PG in the absence of superconductivitiy.

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Figure 1: (a)-(c) Real part of the c-axis infrared conductivity conductivity, σ_{1ab}, of pure and Ni-substituted underdoped $NdBa_2\{Cu_{1-y}Ni_y\}_3O_{6.8}$ single crystals between 10 and 300 K. Arrows mark the onset of the pseudogap at ω^{PG}. Corresponding spectra for Zn substituted crystals are shown in (d) and (e). The evolution of ω^{PG} as a function of Ni content (solid diamonds) and Zn content (open circles) is displayed in (f).

Figure 2: Real part of the c-axis infrared conductivity conductivity, σ_{1ab}, of (a) optimally doped $SmBa_2Cu_{2.6}Ni_{0.4}O_7$ and (b) overdoped $Sm_{0.9}Ca_{0.1}Ba_2Cu_{2.64}Ni_{0.36}O_7$. (c) The doping dependence of the PG energy scale ω^{PG} is shown by solid squares (circles) for pure underdoped (overdoped) crystals and solid diamonds for heavily Ni substituted crystals.